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REMARKS

This reply is in response to the Office Action dated October 17, 2006. Claims 1-4 and 7-33 are pending in the application and claims 1-4, 7-16, 20 and 23-33 stand rejected. Claims 17-19, 21 and 22 have been withdrawn from consideration by the Examiner. Applicant has added new claims 34-78. New claims 34-78 are supported in the specification or the claims as originally filed and therefore, do not add new matter. Entry of the foregoing amendment and reconsideration of the claims is respectfully requested.

Applicants have amended the base claims as shown and added new claims 34-78 to more clearly recite aspects of the invention. The invention relates to metal catalyst precursors having bis cyclopentadienyl ligands, bis bridged cyclopentadienyl ligands, and/or bridged mono cyclopentadienyl ligands, where either the bridge, heteroatom ligand, or both cyclopentadienyl ligands have olefinic unsaturation that can be polymerized by a free radical initiator. None of the references of record teach, show or suggest the claimed invention. In fact, none of the references of record teach, show or suggest precursors having olefinic unsaturation on the bridge. Also, none of the references of record teach, show or suggest precursors having bis cyclopentadienyl ligands or bis bridged cyclopentadienyl ligands where both cyclopentadienyl ligands have at least one olefinic unsaturation that can be polymerized by a free radical initiator as recited in base claims 1, 20, 34, 44, 67, and those dependent therefrom.

In complexes where both cyclopentadienyl (Cp) ligands have at least one olefinic unsaturation substituent that can be polymerized by a free radical initiator, linear polymerization and crosslinking can occur. Crosslinking is not possible where only one of the bis Cps has the olefinic unsaturation substituent.

Both linear polymerization and crosslinking is highly desirable and more than an insignificant advantage. The result is a polymerized catalyst that is less soluble in diluent than a non-crosslinked polymerized catalyst because the crosslinked catalyst forms a blob relative to the non-crosslinked polymerized catalyst. As a result, the less soluble, crosslinked catalyst will produce polymer which is easier to separate from the diluent, less likely to foul the reactor, and overall easier to handle.

Page 26 of 32

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PAGE 29/44 * RCVD AT 3/13/2007 3:49:18 PM [Eastern Daylight Time] * SVR:USPTO-EFAX-2/22 * DNIS:2738300 * CSID:281 834 7413 * DURATION (mm-ss):11-48

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Claims 30-33 stand rejected under 35 U.S.C. § 101 and 35 U.S.C. § 112, first paragraph. Applicant has amended claim 30 to obviate the rejections. Particularly, Applicant has deleted Group III metals from the claims. With regard to Group 5-10 metals, Applicant respectfully disagrees with the Examiner. Group 5-10 metals can undoubtedly have a +4 oxidation state as shown in the selected excerpts from pages 635-636, 715, 737, 757, 776, 896, and 921 of the attached Cotton and Wilkinson textbook. *see* F. Albert Cotton et al., Advanced Inorganic Chemistry, John Wiley & Sons, Inc. (6th Edition 1999). Note that page 636 shows a table where Fe, Co, Ni, Pd are shown as having a +4 oxidation state and the other attached pages (715, 737, 757, 776, 896, and 921) show specific examples of V, Nb Cr, Mo, Mn, Fe, in a +4 state. Therefore, applicant respectfully submits that no amendment is warranted. Withdrawal of the rejection is respectfully requested.

Claims 20, 24 and 30 are objected to. Except for the limitation "TM," Applicant has amended the claims, obviating the objection. Regarding the limitation "TM," the term "TM" within the claimed catalyst formulas is not confusing or ambiguous to anyone of ordinary skill in the art. No one of ordinary skill in the art would confuse "TM" with the term "trademark." Furthermore, Applicant has the right to be his/her own lexicographer. The term "TM" within the catalyst formulas, especially when read in light of the specification, more than adequately describes and enables one skilled in the art to which it pertains how to make and/or use the invention. Accordingly, withdrawal of the objection is respectfully requested.

Claims 14-16, 18-20, 23 and 30 stand rejected under 35 U.S.C. § 112, second paragraph. Applicant has amended the claims in accordance with the Examiner's instructions, obviating the rejection. Accordingly, withdrawal of the rejection is respectfully requested.

Claims 1-4, 7-16, 20 and 24-29 stand rejected under 35 U.S.C. § 102(b) or, in the alternative, under 35 U.S.C. § 103(a) over Schertl et al. (U.S. Patent No. 5,770,755; hereafter "Schertl"). Claims 1-4, 7-16, 20 and 23-33 also stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Schertl.

PATENT

Applicant respectfully traverses the rejection. Schertl does not teach, show or suggest the claimed invention. At the very least, Schertl does not teach, show or suggest a product of a catalyst precursor (having olefinic unsaturated ligands) and at least one monomer reacted in the presence of a free radical initiator, as recited in the claims. Schertl discloses a composition that results from the reaction of an alkali compound, metallocene and a polymeric ligand. *See*, Schertl at col. 6, ll. 19-21 and in the Examples. The ligand is first polymerized to provide a polymeric ligand (with no terminal unsaturation) which is then reacted with a metallocene. *See*, Schertl at col. 3, line 28 through col. 4, line 16. As a result, Schertl does not teach, show or suggest two bridged or unbridged, substituted cyclopentadienyl groups (L_A , L_B) comprising R where R can be polymerized by a free radical initiator (i.e. R has one or more olefinic unsaturated ligands), as required in claim 1-23, 30-43, and 67-78. Schertl also does not teach, show or suggest bridged, mono cyclopentadienyl groups having olefinic unsaturated ligands, as recited in claims 23, 24, 30, and 44, and those dependent therefrom. Schertl also does not teach, show or suggest a bridging group having olefinic unsaturated ligands as recited in claims 1, 23, 24, 30 and 44, as well as those dependent therefrom. For at least these reasons, withdrawal of the rejection and allowance of the claims is respectfully requested.

Claims 1-4, 7-16, 20 and 24-33 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Antberg et al. (U.S. Patent No. 5,169,818; hereafter "Antberg").

Applicant respectfully traverses the rejection. Antberg discloses catalyst systems containing zirconocenes or hafnocenes. *See*, Antberg at col. 1, ll. 67-67 and at col. 2. Antberg does not teach, show or suggest titanium metal complexes as recited in claims 1, 20 and those dependent therefrom. Antberg also does not teach, show or suggest metals in groups 5 to 10 as recited in claims 30 to 33. Antberg also does not teach, show or suggest bridged monocyclopentadienyl catalyst systems, as recited in claim 24 and those dependent therefrom. Withdrawal of the rejection and allowance of the claims is respectfully requested.

Claims 1-4, 7-16, 20 and 24-33 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Antberg as cited above in view of Schertl as cited above. The Examiner states, "It would have been obvious to ... apply the teaching of Schertl to the disclosure of Antberg with

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a reasonable expectation of obtaining a highly-useful olefin polymerization catalyst with the expected benefit of the catalyst being more economical to prepare as well as not fouling polymerization reactors."

Applicant respectfully traverses the rejection on grounds that the Examiner has not established a *prima facie* case of obviousness. "[R]ejections on obviousness grounds cannot be sustained by mere conclusory statements; instead, there must be some articulated reasoning with some rational underpinning to support the legal conclusion of obviousness." In re Lee, 277 F.3d 1338, 1343-46 (Fed. Cir. 2002). In other words, the Examiner must "explain the reasons one of ordinary skill in the art would have been motivated to select the references and to combine them to render the claimed invention obvious." See In re Kahn 04-1616 (Fed. Cir. March 22, 2006). If no explanation is provided, then it is inferred that the Examiner used hindsight. See Id.

Here, the Examiner has simply concluded that the references can be combined "to obtain a highly-useful olefin polymerization catalyst with the expected benefit of the catalyst being more economical to prepare as well as not fouling polymerization reactors." Such "motivation" is merely an unsupported legal conclusion that the combined elements provide an obvious result. Unsupported legal conclusions and impermissible hindsight may not provide a proper basis to support a rejection based on *prima facie* obviousness. Therefore, the Examiner erred in rejecting the claims under 35. U.S.C. §103(a).

Moreover, the Examiner has grossly underestimated the problem solved by the Applicant and grossly over-simplified the Applicant's claimed invention. It has long been established that catalysis is generally considered unpredictable merely from the chemical nature of the catalyst. Corona Co. v. Dovan (USSC 1928) 276 US 358, 369. Catalytic effects are not ordinarily predictable with certainty. In re Doumani et al. (CCPA 1960) 281 F.2d 215, 126 USPQ 408. The effect of a modification of one prior art catalytic process in a manner employed in another prior art process which employs a different catalyst is unpredictable. Ex parte Bergeret al. (POBA 1952) 108 USPQ 236.

In addition, it is well established in the literature and the art that variations in catalyst structures produce substantial polymer differences. Accordingly, there is no expectation that the catalysts of the claimed invention have similar catalytic effects as the catalysts of Antberg and Schertl, each alone or in combination. There is also no expectation that polymers produced from

PATENT

the catalysts of the claimed invention have similar properties as the polymers produced from the catalysts of Antberg and Schertl, each alone or in combination. For at least these reasons, withdrawal of the rejection and allowance of the claims is respectfully requested.

Claims 1-4, 7-16, 20 and 23-33 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Antberg as cited above in view of Chabrand et al. (U.S. Patent No. 5,714,425; hereafter "Chabrand"). The Examiner states, "It would have been obvious to ... apply the teaching of Chabrand to the disclosure of Antberg with a reasonable expectation of obtaining a highly-useful olefin polymerization catalyst with the expected benefit of the polymers made using the catalysts having good processability."

Applicant respectfully traverses the rejection. Antberg has been discussed and distinguished above. Chabrand does not disclose the free radical polymerization of a catalyst precursor with a free radical polymerizable monomer to produce a supported catalysts. In fact, Chabrand's catalysts are supported on silica. Chabrand instead merely discloses that silica supported metallocenes with pendent unsaturations on the Cp rings are useful to polymerize certain olefins. It is clear from reading Chabrand's entire specification that Chabrand does not contemplate, suggest or disclose Applicant's claimed invention no suggest or motivate any modification of Antberg. Withdrawal of the rejection and allowance of the claims is respectfully requested.

Furthermore, it has long been established that catalysis is generally considered unpredictable merely from the chemical nature of the catalyst. Corona Co. v. Dovan (USSC 1928) 276 US 358, 369. Catalytic effects are not ordinarily predictable with certainty. In re Doumani et al. (CCPA 1960) 281 F.2d 215, 126 USPQ 408. The effect of a modification of one prior art catalytic process in a manner employed in another prior art process which employs a different catalyst is unpredictable. Ex parte Bergeret al. (POBA 1952) 108 USPQ 236.

In addition, it is well established in the literature and the art that variations in catalyst structures produce substantial polymer differences. Accordingly, there is no expectation that the catalysts of the claimed invention have similar catalytic effects as the catalysts of Antberg and Chabrand, each alone or in combination. There is also no expectation that polymers produced from the catalysts of the claimed invention have similar properties as the polymers produced

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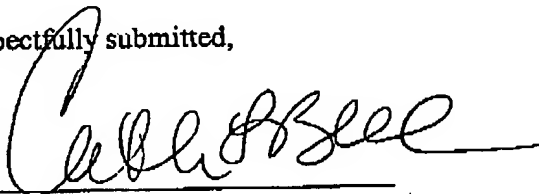
from the catalysts of Antherg and Chabrand, each alone or in combination. For at least these reasons, withdrawal of the rejection and allowance of the claims is respectfully requested.

Having addressed all issues set out in the office action, Applicant respectfully submits that the pending claims are now in condition for allowance. Applicant invites the Examiner to telephone the undersigned attorney if there are any issues outstanding which have not been addressed to the Examiner's satisfaction. A petition for extension of time for filing this response is attached; however, in the event that petition becomes separated from this Response, the Commissioner is hereby authorized to charge counsel's Deposit Account No. 05-1712, for any fees, including extension of time fees and excess claim fees, required to make this response timely and acceptable to the Office.

Respectfully submitted,

Date

March 13, 2007



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P. 35

PATENT

Page 32 of 32

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PAGE 35/44 * RCVD AT 3/13/2007 3:49:18 PM [Eastern Daylight Time] * SVR:USPTO-EFXRF-2/22 * DNIS:2738300 * CSID:281 834 7413 * DURATION (mm-ss):11-48

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16-2 Oxidation State 635

more electrons have been added to the Ac configuration, the 5f orbitals do become definitely the more stable, and since the elements from about americium on do show moderately homologous chemical behavior, it has become accepted practice to call the 15 elements beginning with Ac the *actinide elements*.

There is an important distinction, based on electronic structures, between the three classes of transition elements. For the d-block elements the partially filled shells are *d* shells, 3*d*, 4*d*, or 5*d*. These *d* orbitals project well out to the periphery of the atoms and ions so that the electrons occupying them are strongly influenced by the surroundings of the ion and, in turn, are able to influence the environments very significantly. Thus many of the properties of an ion with a partly filled *d* shell are quite sensitive to the number and arrangement of the *d* electrons present. In marked contrast to this, the 4*f* orbitals in the lanthanide elements are rather deeply buried in the atoms and ions. The electrons that occupy them are largely screened from the surroundings by the overlying shells (5*s*, 5*p*) of electrons; therefore, reciprocal interactions of the 4*f* electrons and the surroundings of the atom or the ion are of relatively little chemical significance. This is why the chemistry of all the lanthanides is so homologous, whereas there are seemingly erratic and irregular variations in chemical properties as one passes through a series of *d*-block elements. The behavior of the actinide element lies between those of the two types just described because the 5*f* orbitals are not so well shielded as are the 4*f* orbitals, although not so exposed as are the *d* orbitals in the *d*-block elements.

16-2 Oxidation State

The concept of oxidation state (or number) plays a more prominent part in describing the chemistry of the transition than it does for the main group elements. This is mainly because in the more ionic bonding that is characteristic of these metallic elements, there is more physical reality to the assignment of such numbers than is the case with the largely covalent chemistry of the main group elements. Of course, even for metallic elements, as oxidation states of +4 or greater are attained, the numbers cannot be given physical significance. Thus while a Ti^{3+} ion has physical reality, there is no real M^{4+} ion and certainly the " Mn^{7+} " in MnO_4^- is purely a formality. Because of this it is best to use, for example, Mn^{VII} rather than Mn^{7+} , that is, a Roman superscript, in designating all oxidation states, even the lower ones.

Generally speaking, and especially for the elements of the first transition series, the highest oxidation state attained in chemically significant circumstances may not correspond to the total number of valence shell electrons. For example, while Sc^{III} , Ti^{IV} , V^{V} , Cr^{VI} , and Mn^{VII} all occur in stable compounds, beyond this the highest oxidation states are lower, namely, Fe^{VI} , Co^{V} , Ni^{IV} , and Cu^{III} .

A graph showing the highest oxidation states of the transition elements is shown in Fig. 16-1. It can be seen that the heavier transition metals can, from Group 7 on, be induced to form compounds in higher states than their first series congeners, but this is almost always confined to their fluorides. In general on descending any group, from 3 to 11, the higher oxidation states become more stable. Thus, Ti^{III} compounds are numerous and important whereas Hf^{III} compounds are relatively rare and Hf^{IV} is predominant. As another example, MnO_4^- is a powerful oxidizing agent, whereas ReO_4^- is not easily reduced.

636 chapter 16/SURVEY OF TRANSITION METAL CHEMISTRY

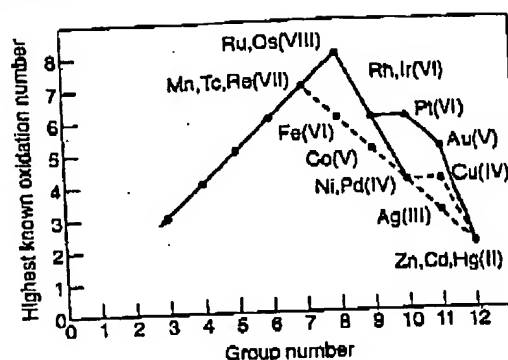


Figure 16-1 Highest known oxidation states for the transition metals. Adapted from M. Kwapp *et al.*, *Inorg. Chem.* 1994, 33, 2122.

16-3 Metal Carbonyls and Kindred Compounds

Although a number of relatively unstable compounds having a CO bonded to metal or metalloid atoms not belonging to the *d*-block have been reported,¹ the formulation of complexes with one or several (up to 6) CO groups bound through carbon atoms to metal atoms is characteristically a property of the transition metals. We shall discuss the compounds in detail in connection with the individual metallic elements, but here some generalizations, especially concerning bonding, will be introduced.

Before discussing bonding as such, we note that the composition of the homoleptic carbonyls is generally given by the so-called 18-electron rule, which states that if each CO group is regarded as a two-electron donor, the sum of the number of electrons in the valence orbitals of the metal atom plus two for each CO group should be equal to 18. In this way formulas such as $M(CO)_6$ ($M = Cr, Mo, W, Mn^+, Re^+$) and $Ni(CO)_4$ are accounted for. When *M* has an odd number of electrons, e.g., Mn, Co, dinuclear species in which there are *M*–*M* bonds are formed and the shared electron pair counts as two electrons for each metal atom. Thus we have $(OC)_2M-M(CO)_2$ ($M = Mn, Tc, Re$) and $Co_2(CO)_8$. As will be noted specifically later, CO groups can also occupy bridging positions. A notable exception to the 18-electron rule is $V(CO)_6$ which has only 17, but such exceptions are rare and the rule extends to mixed organo/carbonyl species, e.g., $C_6H_5Cr(CO)_3$, $C_5H_5Mn(CO)_3$, and $C_5H_5V(CO)_4$.

Let us turn now to the nature of the bond that is normally found in *M*–CO groups. In most cases, it is adequate for practical, everyday purposes to regard a ligand simply as an electron pair donor and to think of the bond to the central atom simply as $L \rightarrow M$. However, there are important classes of compounds for which this simple concept is seriously inadequate. The most prominent examples are the metal carbonyls, metal nitrosyls, and compounds of low-valent metals containing phosphines or isonitriles as ligands.

The explanation for this is believed to be that, as shown in Fig. 16-2, the $C \rightarrow M$ σ dative bond is reinforced by a donation of electrons in the π -type *d* orbitals of *M* to empty π^* orbitals of the CO. Indeed, some calculations ascribe more importance to the π -type “back-bonding” than to the σ donation.

¹J. E. Ellis and W. Beck, *Angew. Chem. Int. Ed. Engl.* 1995, 34, 2489.

17-B-1 The Element 715

behave as Lewis acids, forming adducts with neutral ligands and complex ions with halide ions.

The oxidation states and stereochemistries for vanadium are summarized in Table 17-B-1. We shall discuss the oxidation states V, IV, III, and II individually, and some compounds with mixed oxidation states, metal-metal bonds, organometallic complexes, and bioinorganic chemistry.

17-B-1 The Element

Vanadium has an abundance in Nature of ~0.014%. It is widely spread, but there are a few concentrated deposits. Important minerals are *patronite* (a complex sulfide),

Table 17-B-1 Oxidation States and Stereochemistry of Vanadium

| Oxidation state | Coordination number | Geometry | Examples |
|-----------------|---------------------|--------------------------------|--|
| V^{+1}, d^5 | 6 | Octahedral | $V(CO)_6^+$, $Li[V(bipy)_3] \cdot 4C_4H_8O$ |
| V^0, d^5 | 6 | Octahedral | $V(CO)_6$, $V(bipy)_3$, $V(C_2H_4(PMe_2)_2)_3$ |
| V^{+1}, d^4 | 6 | Octahedral | $[V(bipy)_3]^+$ |
| | | Tetragonal pyramidal | $\eta^5-C_5H_5V(CO)_4$ |
| | 7 | Monocapped octahedral | $[V(CO)_5(PMe_2)_3]^+$, $V(CO)_5(dmpe)_2Cl$ |
| V^{+2}, d^3 | 4 | Almost planar | $[Li(THF)]_2V(2,6\text{-diisopropylphenolate})_4$ |
| | 5 | <i>sp</i> | $(2,6\text{-Ph}_2C_6H_3O)_2V(py)_3$ |
| | 6* | Octahedral | $[V(H_2O)_6]^{2+}$, $[V(CN)_6]^{3-}$ |
| V^{+3}, d^2 | 3 | Planar | $V[N(SiMe_3)_2]_3$, $V[CH(SiMe_3)_3]_3$ |
| | 4 | Tetrahedral | $[VCl_4]^-$ |
| | 5 | <i>tbp</i> | <i>trans</i> - $VCl_3(SMe_2)_2$, $VCl_3(NMe_3)_2$ |
| | 6* | Octahedral | $[V(NH_3)_6]^{3+}$, $[V(C_2O_4)_3]^{3-}$, VF_3 |
| | 7 | Pentagonal bipyramidal | $K_4[V(CN)_7] \cdot 2H_2O$ |
| V^{+4}, d^1 | 4 | Tetrahedral | VCl_4 , $V(NEt_2)_4$, $V(CH_2SiMe_3)_4$ |
| | 5 | Tetragonal pyramidal | $VO(acac)_2$, $PCl_4^+VCl_5^-$ |
| | ? | | $[VO(SCN)_4]^{2-}$ |
| | | <i>sp</i> | $[V_4O_{14}(OH)_2(PhPO_3)_4]^{2+}$, see text |
| | | <i>tbp</i> | $VOCl_2 \text{ trans-}(NMe_3)_2$ |
| | 6* | Octahedral | VO_2 (rutile), K_2VCl_6 , $VO(acac)_2(py)$, $V(acac)_2Cl_2$ |
| V^{+5}, d^0 | 8 | Dodecahedral | $VCl_4(diars)_2$, $V(S_2CMe)_4$ |
| | 4 | Tetrahedral ($C_{\infty v}$) | $VOCl_3$ |
| | 5 | <i>tbp</i> | $VF_5(g)$, $VNCl_2(\text{quinuclidine})_2$ |
| | | <i>sp</i> | $CsVOF_4$ |
| | 6* | Octahedral | $VF_5(s)$, VF_5^- , V_2O_5 (very distorted, almost <i>tbp</i> with one distant O); $[VO_2(ox)_2]^{3-}$, V_2S_5 |
| | 7 | Pentagonal bipyramidal | $VO(NO_3)_3 \cdot CH_3CN$, $VO(Et_2NCS_2)_3$ |

*Most important states.

17-C CHROMIUM: GROUP 6 737

[(NH₃)₆]
protons
molecules
of the

amine ligands the entire series of [Cr(LL)_n]ⁿ with *n* = -1, 0, +1, +2, and +3 is obtained and the compounds are electrochemically interconvertible. In the more electron-rich ones electrons enter orbitals with appreciable (for -1, predominant) ligand character. Complexes containing the [CrNO]²⁺ unit, which contain Cr^I, the Cr^I species [Cr(CO)₂(dmpe)₂]⁺, and arene complexes such as [Cr^I(C₆H₆)₂]⁺, are also known.

The most stable and generally important states are Cr^{II} and Cr^{III}. This dominance of the II and III states that begins here persists through the following transition elements. We shall discuss these states first.

The oxidation states and stereochemistry are summarized in Table 17-C-1.

Table 17-C-1 Oxidation States and Stereochemistry of Chromium

| Oxidation state | Coordination number | Geometry | Examples |
|--|---------------------|-----------------------------------|--|
| Cr ^{-IV} | 4 | Tetrahedral | Na ₂ Cr(CO) ₄ |
| Cr ^{-III} | 5 | <i>tbp</i> | Na ₂ [Cr(CO) ₅] |
| Cr ^{-II} | 6 | Octahedral | Na ₂ [Cr ₂ (CO) ₁₀] |
| Cr ⁰ , <i>d⁶</i> | 6 | Octahedral | Cr(CO) ₆ , [Cr(CO) ₅ I] ⁻ , Cr(bipy) ₃ |
| Cr ^I , <i>d⁵</i> | 6 | Octahedral | [Cr(bipy) ₃] ⁺ , [Cr(CNR) ₄] ⁺ |
| Cr ^{II} , <i>d⁴</i> | 2 | Bent (111°) | Cr[N(Ph)B(mes) ₂] ₂ L ⁺ |
| | 3 | T shape | Cr(OCBu ₃) ₂ LiCl(THF) |
| | 3 | Trigonal planar | [Cr(NP ₂) ₂] ₂ ^d |
| | 4 ^b | Square | CrCl ₂ (Me ₃ py) ₂ , Cr(acac) ₂ |
| | 4 | Distorted tetrahedral | CrCl ₂ (MeCN) ₂ , CrI ₂ (OPPh ₃) ₂ |
| | 5 | <i>tbp</i> | [Cr(Me ₆ tren)Br] ⁺ |
| | 6 | Distorted ^a octahedral | CrF ₃ , CrCl ₃ , CrS |
| | 5 or 6 | Cr—Cr quadruple bond | Cr ₂ (O ₂ CR) ₂ L ₂ , Cr ₂ [(CH ₂) ₂ P(CH ₃) ₂] ₂ , [Cr(CO) ₂ (diars) ₂ XX] |
| Cr ^{III} , <i>d³</i> | 7 | ? | |
| | 3 | Planar | Cr[N(SiMe ₃) ₂] ₃ |
| | 4 | Distorted tetrahedral | [PCL ₄] ⁺ [CrCl ₄] ⁻ , [Cr(CH ₂ SiMe ₃) ₄] ⁻ |
| | 5 | <i>tbp</i> | CrCl ₃ (NMe ₃) ₂ |
| | 5 | <i>sp</i> | CrCl(tmtaa) ^c (see text) |
| Cr ^{IV} , <i>d²</i> | 6 ^b | Octahedral | [Cr(NH ₃) ₆] ³⁺ , Cr(acac) ₃ , K ₃ [Cr(CN) ₆] |
| | 4 | Tetrahedral | Cr(OC ₄ H ₉) ₄ , Ba ₂ CrO ₄ , Cr(CH ₂ SiMe ₃) ₄ |
| | 6 | Octahedral | K ₂ CrF ₆ , [Cr(O ₂) ₂ (en)]H ₂ O, <i>trans</i> -[Cr(NCHMe) ₂ (dmpe) ₂] ²⁺ |
| Cr ^V , <i>d¹</i> | 8 | Dodecahedral | CrH ₂ (dmpe) ₂ |
| | 4 | Tetrahedral | CrO ₄ ²⁻ |
| | 5 | Distorted <i>tbp</i> | CrF ₅ (g) |
| | 5 | <i>sp</i> | CrOCl ₄ |
| | 6 | Octahedral | K ₂ [CrOCl ₄], (CrF ₄) ₆ |
| Cr ^{VI} , <i>d⁰</i> | 8 | Quasi-dodecahedral | K ₂ Cr ₂ (O ₇) ₂ |
| | 4 | Tetrahedral | CrO ₄ ²⁻ , CrO ₂ Cl ₂ , CrO ₃ |

^a Four short and two long bonds.

^b Most stable states.

^c P. P. Power *et al.*, *J. Am. Chem. Soc.* 1990, 112, 1048.

^d S. Gambarotta *et al.*, *Inorg. Chem.* 1989, 28, 812.

^e F. A. Cotton *et al.*, *Inorg. Chim. Acta* 1990, 172, 135.

17-D-1 The Element 757

17-D MANGANESE: GROUP 7

Manganese resembles Ti, V, and Cr in that the highest oxidation state, Mn^{VII} , corresponds to the total number of 3d and 4s electrons. In common with V and Cr the higher oxidation states form $\text{Mn}=\text{O}$ and $\text{Mn}=\text{NBU}'$ multiple bonds. The oxo species are strong oxidants and some are very unstable and explosive.

The oxidation states and stereochemistries are given in Table 17-D-1.

Table 17-D-1 Oxidation States and Stereochemistry of Manganese

| Oxidation state | Coordination number | Geometry | Examples |
|-------------------------------|---------------------|----------------------------|---|
| $\text{Mn}^{-\text{III}}$ | 4 | Tetrahedral | $\text{Mn}(\text{NO})_3\text{CO}$ |
| $\text{Mn}^{-\text{II}}$ | 4 or 6 | Square | $[\text{Mn}(\text{phthalocyanine})\text{F}]^-$ |
| $\text{Mn}^{-\text{I}}$ | 5 | <i>tbp</i> | $\text{Mn}(\text{CO})_5$, $[\text{Mn}(\text{CO})_5\text{PR}_3]^-$ |
| | 4 or 6 | Square | $[\text{Mn}(\text{phthalocyanine})]^-$ |
| Mn^0 | 6 | Octahedral | $\text{Mn}_2(\text{CO})_{10}$ |
| $\text{Mn}^{\text{I}}, d^6$ | 6 | Octahedral | $\text{Mn}(\text{CO})_5\text{Cl}$, $\text{K}_4[\text{Mn}(\text{CN})_6]$, $[\text{Mn}(\text{CNR})_6]^+$ |
| $\text{Mn}^{\text{II}}, d^5$ | 2 | Linear | $\text{Mn}[\text{C}(\text{SiMe}_3)_3]_2$ |
| | 3 | Trig. Planar | $[\text{Li}(\text{thf})_4][\text{Mn}(\text{mes})_3]$ |
| | 4 | Tetrahedral | $[\text{MnCl}_4\text{F}]^-$, $[\text{Mn}(\text{CH}_2\text{SiMe}_2)_4]_n$, $\text{MnBr}_2(\text{OPR}_3)_2$ |
| | 4 | Square | $[\text{Mn}(\text{H}_2\text{O})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$, $\text{Mn}(\text{S}_2\text{CNEt}_2)_2$ |
| | 5 | Distorted <i>tbp</i> | $\text{MnBr}_2[(\text{MeHN})_2\text{CO}]_2$ |
| | | <i>tbp</i> | $[\text{Mn}(\text{trenMe}_6)\text{Br}]\text{Br}$ |
| | 6 | Octahedral | $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Mn}(\text{NCS})_6]^{4-}$ |
| | 7 | NbF_7^- structure | $[\text{Mn}(\text{EDTA})\text{H}_2\text{O}]^-$ |
| | | Pentagonal bipyramidal | $\text{MnX}_2(\text{N}_5 \text{ macrocycle})$ |
| $\text{Mn}^{\text{III}}, d^4$ | 8* | Dodecahedral | $(\text{Ph}_4\text{As})_2\text{Mn}(\text{NO}_3)_4$ |
| | 3 | Trig. Planar | $\text{Mn}[\text{N}(\text{SiMe}_3)_2]_3$ |
| | 4 | Square | $[\text{Mn}(\text{S}_2\text{C}_6\text{H}_5\text{Me})_2]^-$ |
| | 5 | <i>sp</i> | MnXsal_2en , $[\text{bipyH}_2]\text{MnCl}_2$ |
| | 5 | <i>tbp</i> | $\text{MnI}_3(\text{PMe}_3)_2$ |
| | 6 | Octahedral | $\text{Mn}(\text{acac})_3$, $[\text{Mn}(\text{ox})_3]^{3-}$, $\text{MnF}_3(\text{distorted})$, $\text{Mn}(\text{S}_2\text{CNR}_2)_3$ |
| | 7 | | $[\text{Mn}(\text{EDTA})\text{H}_2\text{O}]^-$, $\text{MnH}_3(\text{dmpe})_2$ |
| $\text{Mn}^{\text{IV}}, d^3$ | 4 | Tetrahedral | $\text{Mn}(\text{1-norbornyl})_4$ |
| | 6 | Octahedral | MnO_2 , $\text{MnMe}_4(\text{dmpe})$, MnCl_2^+ , $\text{Mn}(\text{S}_2\text{CNR}_2)_3^+$ |
| $\text{Mn}^{\text{V}}, d^2$ | 4 | Tetrahedral | MnO_4^- , $[\text{Mn}(\text{NBU}')_2(\mu\text{-NBU}')_2]^{2-}$ |
| $\text{Mn}^{\text{VI}}, d^1$ | 4 | Tetrahedral | MnO_4^{2-} , $[\text{Mn}(\text{NBU}')_2(\mu\text{-NBU}')_2]^{2-}$ |
| $\text{Mn}^{\text{VII}}, d^0$ | 3 | Planar | MnO_3 |
| | 4 | Tetrahedral | MnO_4^- , MnO_3F , $\text{MnCl}(\text{NBU}')_3$ |

* For an 8-coordinate N_5 , O_5 cryptate, see K. S. Hagen, *Angew. Chem. Int. Ed. Engl.* 1992, 31, 765.

776 chapter 17 THE ELEMENTS OF THE FIRST TRANSITION SERIES

Table 17-E-1 Oxidation States and Stereochemistry of Iron

| Oxidation state | Coordination number | Geometry | Examples |
|------------------------|---------------------|--------------------------------|--|
| Fe^{-II} | 4 | Tetrahedral | $\text{Fe}(\text{CO})_4^-$, $\text{Fe}(\text{CO})_2(\text{NO})_2$ |
| Fe^0 | 5 | <i>tbp</i> | $\text{Fe}(\text{CO})_5$, $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$, $\text{Fe}(\text{PF}_5)_2$ |
| | 6 | Octahedral(?) | $\text{Fe}(\text{CO})_6\text{H}^+$, $\text{Fe}(\text{CO})_6\text{PPh}_3\text{H}^-$ |
| Fe^I, d^7 | 6 | Octahedral | $[\text{Fe}(\text{H}_2\text{O})_6\text{NO}]^{2+}$ |
| Fe^{II}, d^6 | 2 | Bent | $[\text{Fe}\{(2,4,6\text{-Bu}_3\text{C}_6\text{H}_2)_2\}]$ |
| | 3 | Planar | FeO_3^- , $[\text{Fe}(\text{mcs})(\mu\text{-mes})_2]$ (two 3-coordinated Fe atoms) |
| | 4 | Tetrahedral | FeCl_4^- , $\text{FeCl}_2(\text{PPh}_3)_2$ |
| | 4 | Square | $\text{Fe}(\text{tpp})$ |
| | 5 | <i>tbp</i> | $[\text{FeBr}(\text{Me}_6\text{tren})]\text{Br}$ |
| | 5 | <i>sp</i> | $[\text{Fe}(\text{ClO}_4)(\text{OAsMe}_2)_4]\text{ClO}_4$, $\text{Fe}(\eta^5\text{-OAc})(\text{HB}(3,5\text{-Prfpz})_2)$ |
| | 6 | Octahedral | $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Fe}(\text{CN})_6]^{4-}$ |
| | 8 | Dodecahedral (D_{2d}) | $[\text{Fe}(1,8\text{-naphthyridine})_4](\text{ClO}_4)_2$ |
| Fe^{III}, d^5 | 3 | Trigonal | $\text{Fe}(\text{N}(\text{SiMe}_3)_2)_3$ |
| | 4 | Tetrahedral | FeCl_4^- , Fe^{III} in Fe_3O_4 |
| | 5 | <i>sp</i> | $\text{FeCl}(\text{dtc})_2$, $\text{Fe}(\text{acac})_2\text{Cl}$ |
| | 5 | <i>tbp</i> | $\text{Fe}(\text{N}_3)_3^-$, FeCl_3^- |
| | 6 | Octahedral | Fe_2O_3 , $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$, $\text{Fe}(\text{acac})_3$, FeCl_3 |
| | 7 | Approx. pentagonal bipyramidal | $[\text{FeEDTA}(\text{H}_2\text{O})]^-$ |
| | 8 | Dodecahedral | $[\text{Fe}(\text{NO})_8]^-$ |
| Fe^{IV}, d^4 | 4 | Tetrahedral | $\text{Fe}(1\text{-norbornyl})_4$ |
| | 6 | Octahedral | $[\text{Fe}(\text{diars})_2\text{Cl}_2]^{2+}$ |
| | ? | Organometallic | $(\eta^4\text{-arene})\text{Fe}(\text{H})_2(\text{SiX}_3)_2^a$ |
| Fe^{VI}, d^3 | 4 | Tetrahedral | FeO_4^{2-} |

^aZ. Yao and K. J. Klabunde, *Inorg. Chem.* 1997, 36, 2119.

oxide, commonly known as rust; it affords no protection because it flakes off, exposing fresh metal surfaces. Finely divided Fe is pyrophoric. Iron combines vigorously with Cl_2 on mild heating and also with a variety of other nonmetals including the other halogens, S, P, B, C, and Si. The carbide and silicide phases play a major role in the technical metallurgy of iron.

The metal dissolves readily in dilute mineral acids, in the absence of air and with nonoxidizing acids, to give Fe^{II} . With air present or when warm dilute HNO_3 is used, some of the iron goes to Fe^{III} . Very strongly oxidizing media such as concentrated HNO_3 or acids containing $\text{Cr}_2\text{O}_7^{2-}$ passivate iron. Air-free water and dilute air-free hydroxides have little effect on the metal, but hot concentrated NaOH attacks it.

IRON COMPOUNDS

17-E-2 The Hydroxides and Oxides of Iron

Because of the interrelationships between them it is convenient to discuss the hydroxides and oxides together.

896 chapter 18/THE ELEMENTS OF THE SECOND AND THIRD TRANSITION SERIES

Table 18-B-1 Oxidation States and Stereochemistries of Niobium and Tantalum

| Oxidation state | Coordination number | Geometry | Examples |
|---|---------------------|--|---|
| $\text{Nb}^{-\text{III}}, \text{Ta}^{-\text{III}}$ | 5 | <i>tbp</i> | $[\text{M}(\text{CO})_5]^-$ |
| $\text{Nb}^{-\text{I}}, \text{Ta}^{-\text{I}}$ | 6 | Octahedral | $[\text{M}(\text{CO})_6]^-$ |
| | 7 | ? | $\text{HTa}(\text{PF}_6)_3$ |
| $\text{Nb}^0, \text{Ta}^0, d^5$ | 6 | Octahedral | $\text{Ta}(\text{CO})_6(\text{diphos})$, $17e^-$ compound |
| | | π Complex | $\text{M}(\eta^5\text{-mes})_2$ |
| $\text{Nb}^{\text{I}}, \text{Ta}^{\text{I}}, d^4$ | 7 | π Complex | $(\text{C}_5\text{H}_5)\text{M}(\text{CO})_4$ |
| | 7 | Distorted capped octahedron (nonrigid) | $\text{TaH}(\text{CO})_5(\text{diphos})_2$ |
| $\text{Nb}^{\text{II}}, \text{Ta}^{\text{II}}, d^3$ | | See text | NbO |
| | 6 | Octahedral | $\text{TaCl}_5(\text{dmpe})_2$, $\text{NbCl}_5(\text{py})_4$ |
| $\text{Nb}^{\text{III}}, \text{Ta}^{\text{III}}, d^2$ | 6 | Trigonal prism | LiNbO_3 |
| | | Octahedral | $\text{Nb}_2\text{Cl}_8^{2-}$, $\text{M}_2\text{Cl}_6(\text{SMe}_2)_2$ |
| | 7 | Complex | $\text{TaCl}_5(\text{CO})(\text{PMe}_2\text{Ph})_3 \cdot \text{EtOH}$ |
| | 8 | Dodecahedral | $\text{K}_3[\text{Nb}(\text{CN})_8]$ |
| $\text{Nb}^{\text{IV}}, \text{Ta}^{\text{IV}}, d^1$ | 6 | Octahedral | $(\text{NbCl}_6)_3$, TaCl_6py_2 , MCl_6^{2-} |
| | 7 | Distorted pentagonal bipyramidal | K_2NbF_7 |
| | 7 | Capped octahedron | $\text{MCl}_4(\text{PMe}_2)_3$ |
| | 8 | Nonrigid in solution | $\text{TaH}_4(\text{diphos})_2$ |
| | | Square antiprism | $\text{Nb}(\beta\text{-dike})_4$, $\text{M}_2\text{Cl}_6(\text{PMe}_2)_4$, $\text{Nb}(\text{SCN})_4(\text{dipy})_2$ |
| | | Dodecahedral | $\text{K}_4\text{Nb}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$ |
| | | π Complex | Cp_2NbMe_2 |
| $\text{Nb}^{\text{V}}, \text{Ta}^{\text{V}}, d^0$ | 4 | Tetrahedral | ScNbO_4 |
| | 5 | <i>tbp</i> | $\text{MCl}_5(\text{vapor})$, TaMe_5 , $\text{Nb}(\text{NR}_2)_5$ |
| | | Distorted tetragonal pyramid | $\text{Nb}(\text{NMe}_2)_5$ |
| | 6 | Octahedral | NaMO_3 (perovskite), $\text{NbCl}_5 \cdot \text{OPCl}_3$, $\text{TaCl}_5 \cdot \text{S}(\text{CH}_3)_2$, TaF_5 , NbOCl_3 , M_2Cl_{10} , MCl_6 |
| | 6 | Trigonal prism | $[\text{M}(\text{S}_2\text{C}_6\text{H}_4)_3]^-$ |
| | 7 | Distorted pentagonal bipyramidal | $\text{NbO}(\text{S}_2\text{CNEt}_2)_3$ |
| | | Pentagonal bipyramidal, fluxional | $\text{STa}(\text{S}_2\text{CNEt}_2)_3$, $\text{Ta}(\text{NMe}_2)(\text{S}_2\text{CNMe}_2)_3$, $(\text{S}_2\text{CNR}_2)_2\text{TaMe}_3$ |
| | 8 | Bicapped trigonal prism | $[\text{Nb}(\text{trop})_4]^+$ |
| | | Square antiprism | Na_3TaF_8 |
| | | Dodecahedral | $\text{Ta}(\text{S}_2\text{CNMe}_2)_3$ |
| | 9 | π Complex | $(\eta^5\text{-C}_5\text{H}_5)_2\text{TaH}_3$ |

Table 18-C-1 Oxidation States and Stereochemistry of Molybdenum and Tungsten

| Oxidation state | Coordination number | Geometry | Examples |
|---|---------------------|----------------------------------|---|
| Mo ^{II} , W ^{II} | 5 | ? | [Mo(CO) ₅] ²⁻ |
| Mo ⁰ , W ⁰ , d ⁶ | 6 | Octahedral | W(CO) ₆ , (py) ₃ Mo(CO) ₃ , [Mo(CO) ₆] ²⁻ , [Mo(CN) ₆ NO] ⁴⁻ , Mo(N ₂) ₂ (diphos) ₂ |
| Mo ^I , W ^I , d ⁵ | 6 ^a | π Complex | (C ₆ H ₅) ₂ Mo ⁺ , η ⁵ -C ₅ H ₅ MoC ₆ H ₅ , [η ⁵ -C ₅ H ₅ Mo(CO) ₃] ₂ |
| | 7 ^a | | MoCl(N ₂)(diphos) ₂ |
| | 6 | ? | |
| Mo ^{II} , W ^{II} , d ⁴ | 5 | M—M quadruple bond | Mo ₂ (O ₂ CR) ₄ , [Mo ₂ Cl ₄] ⁴⁻ , W ₂ Cl ₄ (dppe) ₂ |
| | 6 | Octahedral | Mo(diars) ₂ X ₂ , trans-Me ₂ W(PMe ₃) ₄ |
| | 7 ^a | π Complex | η ⁵ -C ₅ H ₅ W(CO) ₃ Cl |
| | | Capped trigonal prism | [Mo(CNR) ₃] ³⁻ |
| | | Pentagonal bipyramidal | [Mo(CN) ₅] ³⁻ |
| | | 4:3 | [WBr(CO) ₂ (PR ₃) ₂] ₂ C ₂ O ₄ |
| Mo ^{III} , W ^{III} , d ³ | 9 | Cluster compounds | Mo ₆ Cl ₁₂ , W ₆ Cl ₁₂ |
| | 4 | M—M triple bond | Mo ₂ (OR) ₄ , W ₂ (NR) ₄ , [Mo ₂ (HPO ₄) ₄] ²⁻ |
| | 6 | Octahedral | [Mo(NCS) ₆] ³⁻ , [MoCl ₆] ³⁻ , [W ₂ Cl ₂] ³⁻ |
| | 7 | ? | [W(diars)(CO) ₂ Br] ⁺ |
| Mo ^{IV} , W ^{IV} , d ² | 8 | Dodecahedral (?) | [Mo(CN) ₄ (H ₂ O)] ⁴⁻ |
| | 8 ^a | π Complex | (η ⁵ -C ₅ H ₅) ₂ WH ₂ , (η ⁵ -C ₅ H ₅) ₂ MoCl ₂ |
| | 9 ^a | π Complex | (η ⁵ -C ₅ H ₅) ₂ WH ₂ |
| | 4 | Tetrahedral | Mo(NMe ₂) ₄ , Mo(SBu ⁿ) ₄ , Mo[TeSi(SiMe ₃) ₃] ₄ ^b |
| | 6 | Octahedral | [Mo(NCS) ₆] ²⁻ , [Mo(diars) ₂ Br] ²⁺ , WBr ₄ (MeCN) ₂ , MoOCl ₂ (PR ₃) ₂ |
| | 6 | Trigonal prism | MoS ₂ |
| | 8 | Dodecahedral or square antiprism | [M(CN) ₄] ⁴⁻ , Mo(S ₂ CNMe ₂) ₄ , M(picolate) ₄ |
| Mo ^V , W ^V , d ¹ | 5 | trp | MoCl ₅ (g) |
| | 6 | Octahedral | Mo ₂ Cl ₁₀ (s), [MoOCl ₃] ²⁻ , WF ₆ |
| | 8 | Dodecahedral or square antiprism | [M(CN) ₆] ³⁻ |
| Mo ^{VI} , W ^{VI} , d ⁰ | 4 | Tetrahedral | MO ₂ ²⁺ , MoO ₂ Cl ₂ , WO ₂ Cl ₂ |
| | 5 [?] | ? | WOCl ₄ , MoOF ₄ |
| | 6 | Octahedral | MoO ₆ , WO ₆ in polyacids, WCl ₆ , Mo(OMe) ₆ , WOCl ₄ (s), MoF ₆ , [MoO ₂ F ₄] ²⁻ , MoO ₃ (distorted), WO ₃ (distorted) |
| | 7 | Distorted trigonal prism | W(CH ₃) ₆ |
| | | Distorted pentagonal bipyramid | WOCl ₄ (diars), K ₂ [MoO(O ₂) ₂ (ox)] |
| | 8 | ? | MoF ₆ ²⁻ , WF ₆ ²⁻ , [WMe ₆] ²⁻ |
| | 9 | ? | WH ₆ (Me ₂ PhP) ₃ |

^aAssuming η⁶-C₆H₆ or η⁵-C₅H₅ occupy three coordination sites.

^bJ. Arnold et al., *Chem. Commun.* 1996, 2565.

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